PART ONE
ISOPROPYL ALKYLATIONS OF DIAMINOMESITYLENE

PART TWO
RESTRICTED ROTATION IN DERIVATIVES OF DIAMINODURENE

BY

NILS KEITH NELSON

B.S., Missouri School of Mines and Metallurgy, 1946
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
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PART ONE

ISOPROPYL ALKYLATIONS OF DIAMINOMESITYLENE

Introduction

Certain alkyl derivatives of diaminomesitylene have been prepared which possess two points of asymmetry because of restricted rotation about the C-N bonds between the amine nitrogens and the adjacent carbon atoms of the benzene ring. It was found that N,N′-dialkyl-N,N′-dibenzenesulfonyldiaminomesitylenes could be prepared by alkylating basic solutions of N,N′-dibenzenesulfonyldiaminomesitylene with *n*-alkyl halides, and the product could be separated into *cis*- and *trans*- isomers by fractional crystallization (1,2). The dimethyl derivative was also prepared by adding benzenesulfonyl chloride to N,N′-dimethyldiaminomesitylene (2). However, it was reported that when the diethyl derivative of diaminomesitylene was treated with benzenesulfonyl chloride, one ethyl group was lost, and N-ethyl-N,N′-dibenzenesulfonyldiaminomesitylene was formed (1).

The purpose of this investigation was to extend the study to secondary alkyl derivatives of diaminomesitylene.

Discussion Of Results

It was found that diaminomesitylene could be alkylated with isopropyl bromide in an alcoholic medium. The reaction proceeded in a stepwise fashion. The monoisopropyl derivative could be prepared by normal alkylating conditions, but the second phase of the alkylation required the use of pressure vessels.

The compound was purified by converting it to N,N′-dinitroso-N,N′-di-isopropyldiaminomesitylene, which was isolated and later reduced back to di-isopropyldiaminomesitylene.

Benzenesulfonyl chloride reacted with N,N′-di-isopropyldiaminomesitylene in a stepwise fashion to produce first,

N-benzenesulfonyl-N,N′-di-isopropyldiaminomesitylene and second, N,N′-di-isopropyl-N,N′-dibenzenesulfonyldiaminomesitylene. The latter compound could be separated into *cis-* and *trans-* isomers. However, only a trace of the low melting isomer could be isolated. No N-isopropyl-N,N′-dibenzenesulfonyldiaminomesitylene was produced by the reaction.

A basic solution of N,N′-dibenzenesulfonyldiaminomesitylene was alkylated with a mixture of isopropyl bromide and isopropyl iodide. However, the yield of product was low, and only the high melting isomer of the N,N′-di-isopropyl derivative was formed.

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PART TWO

RESTRICTED ROTATION IN DERIVATIVES OF DIAMINODURENE

Introduction

In Part I of this abstract it was stated that several compounds of the general structure, N,N′-dialkyl-N,N′-dibenzenesulfonyldiaminomesitylene had been prepared, and that these compounds had been separated into *cis-* and *trans-* isomers.

In this study it was proposed to prepare several similar compounds in the diaminodurene series and determine if they, too, possessed restricted rotation.

Discussion Of Results

Basic solutions of N,N′-dibenzenesulfonyldiaminodurene

were easily alkylated with methyl iodide, ethyl bromide, and benzyl chloride. All three dialkyl derivatives could be separated into *cis-* and *trans-* isomers. The diethyl derivative was also prepared by adding benzenesulfonyl chloride to N,N′-diethyldiaminodurene.

Attempts to prepare N,N′-dicarboxyalkyl derivatives of N,N′-dibenzenesulfonyldiaminodurene by alkylating a basic solution of the sulfonamide were unsuccessful. However, it was found that acrylonitrile would add to the sulfonamide in the presence of an equivalent of benzyltrimethylammonium hydroxide. The reaction proceeded in a stepwise manner. Once the sulfonamide was converted directly to N,N′-dicyanoethyl-N,N′-dibenzenesulfonyldiaminodurene, and the product was separated into *cis-* and *trans-* isomers. However, subsequent reactions with acrylonitrile gave only the monocyanoethylated compound, and when it reacted with acrylonitrile, only one isomer of the dialkyl product was formed.

The isomers of N,N′-dicyanoethyl-N,N′-dibenzenesulfonyldiaminodurene were easily hydrolyzed to the corresponding acids. The high melting acid reacted with acetic anhydride to give the mixed anhydride, N,N′-diacetylcarboxyethyl-N,N′-dibenzenesulfonyldiaminodurene.

The low melting isomers of the N,N′-dialkyl-N,N′-dibenzenesulfonyldiaminodurenes were converted to the corresponding high melting isomers when heated above their melting points.

VITA

The author was born in Leadwood, Missouri on November 10, 1926. He attended the public schools of Bonne Terre and Farmington, Missouri and graduated from high school in May, 1943. The following month he entered the Missouri School of Mines where he completed the requirements for the degree of Bachelor of Science in chemical engineering in February, 1946. He has been enrolled in the Graduate School at the University of Illinois since March, 1946.

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